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GROWTH AND CHARACTERIZATION OF CARBON NANOTUBES ON CONSTANTAN (Cu–Ni–Mn ALLOY) METALLIC SUBSTRATES WITHOUT ADDING ADDITIONAL CATALYSTS (POSTPRINT)

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14. ABSTRACT
In this study, metallic constantan (Cu55–Ni44–Mn1 wt %) alloy substrates were investigated as an alternate choice of substrates to grow carbon nanotubes (CNTs). No additional catalysts were used other than the as-rolled and annealed substrates to process CNTs on them. High density CNT growth was observed to take place on these substrates when suitable conditions were used in a thermal chemical vapor deposition (CVD) furnace with C_2H_2 as the carbon precursor. Scanning electron microscopy and transmission electron microscopy on these samples indicated the presence of several micron long CNTs ranging in 20 to 100 nm in diameter. Raman spectra taken from the samples confirmed the presence of G band peaks (peak at ~ 1580 cm^{-1}) and D band peaks (peak at ~1320 cm^{-1}) commonly observed in CVD grown multiwall CNT samples with varying intensity ratios depending on the processing conditions.

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Growth and characterization of carbon nanotubes on constantan (Cu–Ni–Mn alloy) metallic substrates without adding additional catalysts

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In this study, metallic constantan (Cu55–Ni44–Mn1 wt %) alloy substrates were investigated as an alternate choice of substrates to grow carbon nanotubes (CNTs). No additional catalysts were used other than the as-rolled and annealed substrates to process CNTs on them. High density CNT growth was observed to take place on these substrates when suitable conditions were used in a thermal chemical vapor deposition (CVD) furnace with C_2H_2 as the carbon precursor. Scanning electron microscopy and transmission electron microscopy on these samples indicated the presence of several micron long CNTs ranging in 20–100 nm in diameter. Raman spectra taken from the samples confirmed the presence of *G* band peaks (peak at $\sim$1580 cm^{-1}) and *D* band peaks (peak at $\sim$1320 cm^{-1}) commonly observed in CVD grown multiwall CNT samples with varying intensity ratios depending on the processing conditions. © *2008 American Vacuum Society.* [DOI: 10.1116/1.2841520]

INTRODUCTION

Carbon nanotubes first imaged by Iijima in 1991[1] are now being investigated worldwide for many potential applications in several fields such as electronic, thermal, biomedical, composite, field emission, sensors, etc., due to their unique properties.[2] Although significant progress has been made in understanding the growth mechanism of carbon nanotubes (CNTs), the control over the chirality of CNTs still remains as a significant challenge and an active continuing area of research. While there are several methods of manufacturing CNTs[3,4] being investigated, one of the common methods used to grow CNTs on a variety of substrates is chemical vapor deposition (CVD) using C_2H_2 or CH_4 as precursors.

Metallic nanoparticles such as Fe, Ni, etc., are deposited on the substrates prior to the CNT growth to act as catalysts during the CVD process.[3] However, in this approach the adhesion of CNTs to the substrates can sometimes be problematic as the nanoparticles are not integrated into the substrate. One means to overcome this problem is the use of metallic substrates to grow CNTs without the additional processing step of adding nanoparticle catalysts. In the literature pure Ni substrates have been reported to be used to grow CNTs (Refs. 5 and 6) with some success. In some other studies, Ni and other metallic substrates were used with additional catalysts to improve the density of CNTs.[7,8] Stainless steel[9] or aluminum[10] was also used as substrates but were given prior treatments to create catalyst islands on these substrates to grow CNTs.

In this present study, rolled and annealed commercially available constantan (Cu55–Ni44–Mn1 wt %) alloy substrates with a well defined grain structure were investigated as an alternate substrate to grow CNTs. No additional catalysts were added to the substrates. Experiments were conducted to determine if it is possible to grow high density CNTs on these substrates. As opposed to a pure Ni metal, an alloy with the precipitates of the alloying additions and other defects such as grain boundaries, etc., may provide the necessary and appropriate nucleation sites for the high density of CNT growth.

EXPERIMENT

A vertical thermal CVD reactor was built in house to grow CNTs. Initially the CNTs were grown at atmospheric pressure using C_2H_2/argon mixtures. Prior to deposition, the quartz tube of the reactor was purged with argon gas with a flow rate of 300 SCCM (SCCM denotes cubic centimeter per minute at STP), for 30 min. The temperature was then ramped up to 700 °C in argon gas flowing at a rate of 300 SCCM. The CNTs were grown on different substrates in an argon/acetylene (10%) gas flowing at a rate of 30–300 SCCM for 2–10 min. The precursor gas was subsequently purged using argon gas at a flow rate of 300 SCCM for 30 min at the end of the growth, and the furnace was cooled down to room temperature in flowing argon gas at 300 SCCM.

To determine the quality of CNTs grown in the home built CVD reactor, CNTs were grown on Si substrates decorated with Ni islands. Pulsed laser deposition (PLD) was used to

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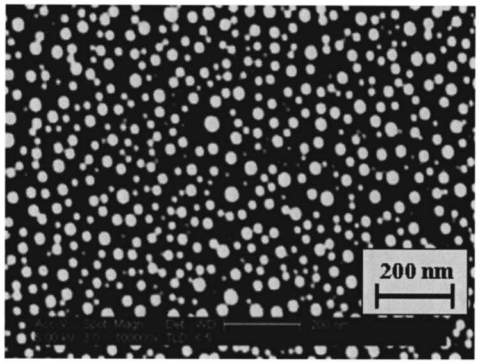
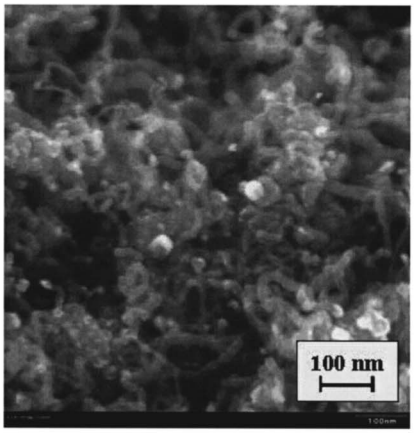
deposit Ni islands on Si substrates. A Lambda Physik KrF excimer laser (wavelength $\lambda = 248$ nm) was used to deposit Ni films in a Neocera PLD chamber. The deposition was carried out using an energy density of 2 J/cm^2 at a 20 Hz repetition rate at room temperature in an argon gas pressure of 300 mtorr. A thin film of Ni was deposited for 30 s to 3 min, and then the Si substrate was annealed at 750 °C for 30 min in Ar/4%H_2 gas mixture to break the film into islands. These substrates as well as several as-rolled and annealed (500 °C, 3 h and 1200 °C for 2 h) constantan substrates were investigated for CNT growth. It has been shown earlier that different heat treatments would produce different degrees of (100) texture and grain size in constantan substrates.[11] The annealed as well as, as-rolled metallic substrates were roughened by either mechanical grinding using 400–600 grit SiC paper or by ion milling for 10–15 min. The mechanically ground substrates were thoroughly cleaned before they were used for the CNT growth. Initially they were cleaned in an ultrasonic cleaner in acetone for 5 min and then further cleaned in a separate beaker in isopropyl alcohol for 5 more min. Ion milled substrates were not sonicated like ground substrates as no contact with foreign materials occurred in this process.

Scanning electron micrographs of CNTs grown on various substrates were taken using a FEI Sirion scanning electron microscope as well as a Hitachi S-4800 high resolution scanning electron microscope. Transmission electron microscopy was done using a Philips CM200 electron microscope as well as Hitachi H-7600 transmission electron microscope. Raman spectroscopy was performed using a Renishaw in Via reflex spectrometer system. The excitation source was a 300 mW red laser of wavelength of 785 nm.



(a)



(b)

FIG. 1. (a) Scanning electron micrograph of a Si substrate sample with Ni islands deposited using a pulsed laser ablation method and then annealed. (b) Scanning electron micrograph showing CNTs grown on a Si substrate sample decorated with Ni islands prior to growth, as shown in Fig. 1(a).

RESULTS AND DISCUSSION

Figure 1(a) shows the scanning electron microscopy (SEM) photomicrograph of a Si substrate with Ni islands deposited by PLD method. After the annealing treatment, Ni islands of 10–50 nm were formed as can be seen in this micrograph. Figure 1(b) shows the plan view of the CNTs grown on the same substrate. A very high density of several microns long CNTs of ~20–50 nm diameters can be seen in this micrograph. Figure 2 shows the cross-sectional SEM of a similar sample. CNTs were found to be random but extend to more than 2.5 μm in length. No preferential alignment was noticed due to a low density of islands. In addition, the turbulence of the precursor gases in a vertical CVD reactor is thought to be partly responsible for the lack of alignment of the CNTs. The processing parameters are not yet optimized to reduce the Ni island size or to produce the CNTs of uniform diameter. However, these results on the Si substrates served the purpose of evaluating the present CVD reactor with the aforementioned set of processing conditions for use in investigating whether constantan can be used as a substrate.

Figure 3 shows the CNTs grown on rolled and low temperature annealed (500 °C, 3 h) constantan substrates of a 50 μm thickness when similar processing conditions are used as for the Si substrate. A very high density of CNTs of varying diameters (20–100 nm) can be seen to grow on these substrates similar to the Si substrates decorated with Ni islands, as shown in Fig. 1(b). Even though the substrate was roughened using a 600 grit SiC paper as mentioned before, it was thoroughly cleaned in an ultrasonic cleaner prior to the CVD growth to prevent any residual particles from remain-

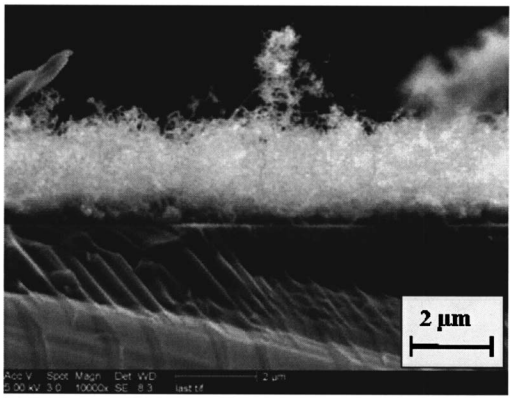


FIG. 2. Cross-sectional SEM of the same sample showing the thickness of the CNT mat grown on the Si substrate with PLD deposited Ni islands.

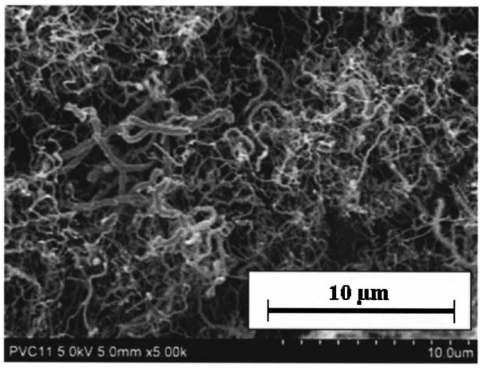


FIG. 3. SEM micrograph of CNTs grown on rolled and low temperature annealed (500 °C, 3 h), mechanically ground, constantan substrate.

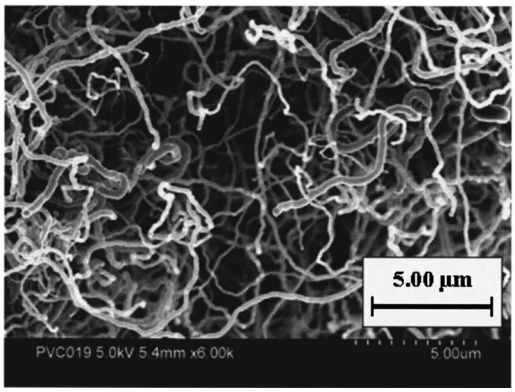


FIG. 5. SEM micrograph of CNTs grown on as-rolled, mechanically ground constantan substrate.

ing on the substrate. Therefore, it is believed that the Ni and Mn that are integral to the constantan substrate serve as the catalysts to grow the CNTs and not the SiC residue.

Figure 4 shows CNTs grown on high temperature annealed constantan substrate (1200 °C, 2 h) that were roughened using an ion milling process. The CNTs grown on this substrate are much denser and narrower in diameter than compared to the substrates that were grown on the mechanically polished substrate, as shown in Fig. 3. Although ion milling is not an economical way to roughen substrate surfaces, the present results indicate that surface roughening/preparation plays an important role in determining the diameter of the CNTs. It further justifies the previous hypothesis that SiC residue of the mechanically polished substrate does not play a major role if any in the CNT growth. It was also noted that CNTs can be processed on as-rolled constantan substrate with a different surface texture than the annealed substrates, as shown in Fig. 5. The ability to provide partial optimization of the CNTs produced to a desired quality through proper substrate treatment is presently under further investigation.

Figure 6 shows the transmission electron microscopy (TEM) images of the CNTs grown on the constantan substrates. While the tubular nature is clear from the pictures, the inner walls were not able to be imaged clearly. It appears that there could be some amorphous carbon present on the surface of the tubes with the present set of conditions used and probably interferes with the imaging of the inner walls. Experiments are underway to reduce the amorphous carbon on the surface of the CNTs and to improve the TEM sample preparation. The TEM figure shown in Fig. 7 indicates that tip growth in addition to root growth can potentially occur in the CNTs grown on the metallic substrates. Similar to other substrates, the constantan substrate used in this sample was initially roughed by using a 400 grit SiC paper and then ultrasonically cleaned in acetone and isopropyl alcohol for 5 min before using for CNT growth.

The Raman spectra show the presence of the G band (peak at $\sim$1580 cm^{-1}) and D band (peak at $\sim$1320 cm^{-1}) peaks commonly observed for carbon materials in all the samples processed on the metallic substrates with varying relative intensities. The intensity of G/D seems to vary showing very high G/D ratio in as-rolled substrates and very

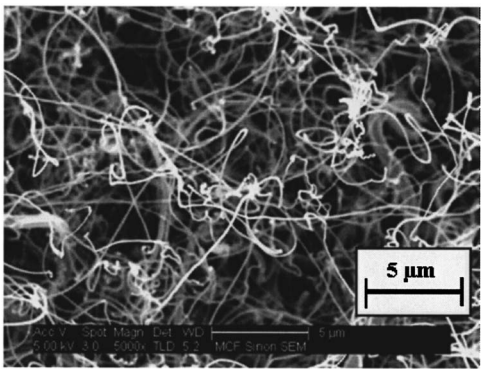


FIG. 4. SEM micrograph of CNTs grown on rolled and high temperature annealed (1200 °C, 2 h), ion milled constantan substrate.

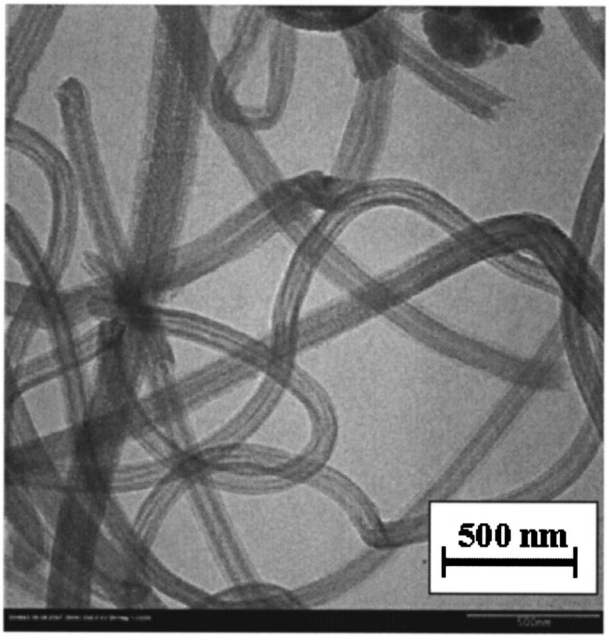


FIG. 6. Transmission electron micrograph of CNTs grown on high temperature annealed (1200 °C, 2 h), ion milled constantan substrates.

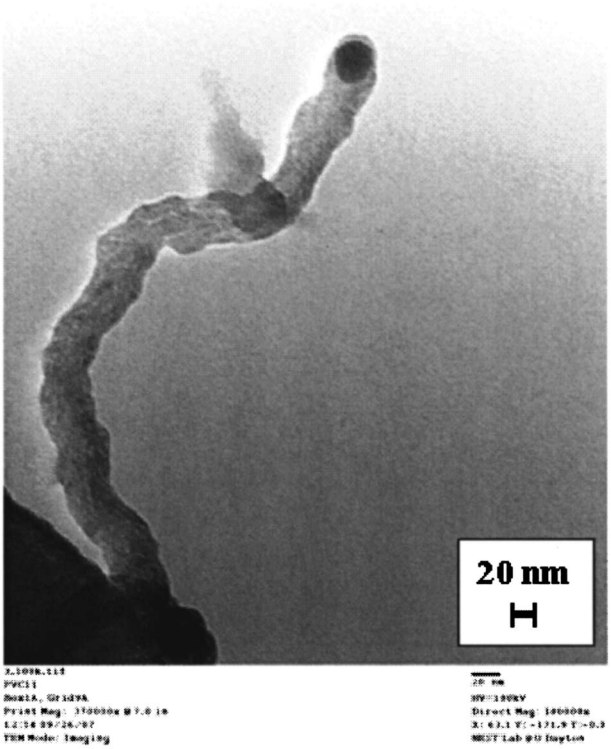


FIG. 7. Transmission electron micrograph of CNTs showing tip growth mechanism may also be possible in the constantan substrates.

low value for ion milled roughened constantan substrates, as shown in Fig. 8. This further indicates that the surface preparation of the substrates is very important in determining the quality of the CNTs in constantan substrates. Simple treatments of mechanical grinding/ion milling processes could form active nucleation sites on the surface. Formation of nanoparticles is also possible due to these treatments as shown in Fig. 7 that help in the tip growth of CNTs. Even so, all the substrates indicate that the constantan can be used to produce CNTs without an additional treatment of depositing external catalyst particles.

CONCLUSIONS

High density CNTs were grown on Si substrates with Ni islands (deposited by PLD) in a vertical CVD reactor using C_2H_2 precursor as well as on as-rolled and annealed constantan substrates. It is demonstrated that CNTs can be grown in the same reactor on the as-rolled and as-annealed constantan substrates without adding any additional catalyst islands in

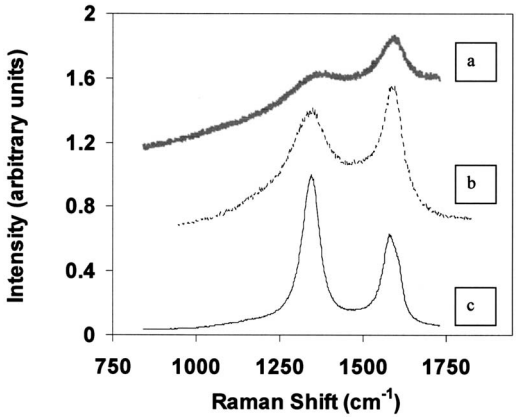


FIG. 8. Raman spectra of CNTs grown on three different samples. (a) Constantan substrate annealed and then ion milled to roughen. (b) Constantan substrate annealed and mechanically ground to roughen. (c) Constantan substrate in as-rolled condition and mechanically grinded.

using similar conditions as used for the Si substrate with islands. The as grown CNTs on the constantan metallic substrates were random, several microns long, and had diameters ranging from 20 nm to 100 nm. The CNTs also show both tip and root growth mechanisms on these constantan substrates.

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